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(71) Applicant *(for all designated States except US)*: ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: DE MERINGO, Alain [FR/FR]; 294, rue Saint-Jacques, F-75005 Paris (FR). BATTIGELLI, Jean [FR/FR]; 17, rue E.-Vaillant, F-60290 Rantigny (FR). FURTAK, Hans [DE/DE]; Im Oberkämmerer 35, D-67346 Speyer am Rhein (DE).

(74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 Munich (DE).

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(54) Title: GLASS-FIBER COMPOSITIONS

(57) Abstract

A biologically degradable glass-fiber composition characterized by the following constituents in percent by weight: SiO_2 45 to 60, Al_2O_3 less than 2, CaO + MgO 10 to 16, Na_2O + K_2O 15 to 23, B_2O_3 10 to 18, P_2O_5 0 to 4, BaO 0 to 1, diverse 0 to 2.

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Glass-fiber compositions

The present invention relates to a glass-fiber composition that is biologically degradable.

The prior art describes some glass-fiber compositions which are said to be biologically degradable.

The biological degradability of glass-fiber compositions is of great importance because various studies point out that some glass fibers with very small diameters in the range of less than 3 microns may be carcinogenic, while biologically degradable glass fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the glass fibers, or the products produced therefrom, the resistance of the glass fibers and the processibility of the glass-fiber composition. For example glass fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the glass-fiber composition must permit processibility by known methods for producing glass fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel glass-fiber composition that is characterized by biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a glass-fiber composition that contains considerable amounts of alkali oxides and boron oxide, as well as optionally aluminum oxide.

It has turned out that such a glass-fiber composition fulfills the combination of the necessary properties, namely

biological degradability, resistance to moisture and good processibility.

The object of the invention is a glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	15 to 23
B_2O_3	10 to 18
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions are processible by the centrifugal technique. The obtained fibers have good resistance to moisture. Surprisingly enough, the glass-fiber compositions show biological degradability. The mean fiber diameter is preferably less than 10 microns and is in particular between 2.5 and 5 microns.

The inventive glass-fiber compositions preferably have the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	more than 18
B_2O_3	less than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

According to a further preferred embodiment the inventive glass-fiber compositions have the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	less than 18
B_2O_3	more than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

The inventive glass-fiber compositions preferably have less than 57 percent by weight silicon dioxide, in particular less than 56.5 percent by weight.

By adding aluminum oxide one can obtain an improvement in moisture-resistance. The inventive compositions are therefore preferably given at least 0.1 percent by weight, in particular at least 0.5 percent by weight, and usually less than 1.5 percent by weight aluminum oxide.

Biological degradability can be increased by the addition of phosphorus pentoxide. The inventive compositions therefore preferably contain at least 0.1 percent by weight P_2O_5.

According to a further preferred embodiment the composition contains less than 2 percent by weight magnesium oxide.

The moisture-resistance of the inventive glass-fiber compositions was determined by a standard method known as the DGG method. In the DGG method 10 g finely ground glass with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount of glass dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested glass.

The biological degradability of the inventive glass compositions was tested by introducing 1 g of the glass

powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

NaCl	6.78
NH_4Cl	0.535
$NaHCO_3$	2.268
$NaH_2PO_4H_2O$	0.166
(Na_3 citrate) $2H_2O$	0.059
Glycine	0.450
H_2SO_4	0.049
$CaCl_2$	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO_2 in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Example 1

A glass of the following composition in percent by weight was melted:

SiO_2	56.0
Al_2O_3	1.0
CaO	9.0
MgO	4.0
Na_2O	18.0
K_2O	1.0
B_2O_3	10.5
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 2

A glass with the following composition in percent by weight was melted:

SiO_2	55.0
Al_2O_3	1.0
CaO	9.0
MgO	4.0
Na_2O	18.0
K_2O	1.0
B_2O_3	10.5
P_2O_5	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 40 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 3

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.0
MgO	3.5
Na_2O	17.8
K_2O	0.2
B_2O_3	12.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 50 mg/g was determined.

The above-described test for biological degradability yielded a value of 550.

Example 4

A glass with the following composition in percent by weight was melted:

SiO_2	56.5
Al_2O_3	0.5
CaO	8.0
MgO	3.5
Na_2O	17.8
K_2O	0.2
B_2O_3	12.0
P_2O_5	1.0
Diverse	0.5.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 50 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 5

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.1
MgO	3.6
Na_2O	17.25
K_2O	0.35
B_2O_3	12.4
Diverse	0.3.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 6

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.3
MgO	1.8
Na_2O	18.6
K_2O	0.4

B_2O_3	11.5
BaO	1.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 7

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.3
MgO	1.8
Na_2O	17.1
K_2O	0.4
B_2O_3	13.0
BaO	1.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Example 8

A glass with the following composition in percent by weight was melted:

SiO_2	57.5
Al_2O_3	0.5
CaO	8.4
MgO	1.7
Na_2O	17.0
K_2O	0.5
B_2O_3	14.0
Diverse	0.4.

These glass compositions could be processed by the centrifugal technique.

Using the above-described DGG method a value of 30 mg/g was determined.

The above-described test for biological degradability yielded a value of 600.

Claims

1. A glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	15 to 23
B_2O_3	10 to 18
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

2. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	more than 18
B_2O_3	less than 12
P_2O_5	0 to 4
BaO	0 to 1
Diverse	0 to 2.

3. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	45 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	less than 18
B_2O_3	more than 12
P_2O_5	0 to 4

BaO	0	to	1
Diverse	0	to	2.

4. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	47	to	57
Al_2O_3	less than 2		
CaO + MgO	12	to	15
$Na_2O + K_2O$	16	to	20
B_2O_3	10	to	16
P_2O_5	0	to	2
BaO	0	to	1
Diverse	0	to	2.

5. The glass-fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO_2	52	to	60
Al_2O_3	0	to	1.5
CaO + MgO	11	to	12.5
$Na_2O + K_2O$	16	to	18.5
B_2O_3	10	to	14
P_2O_5	0	to	1
BaO	0	to	1
Diverse	0	to	2.

6. The glass-fiber composition of any of claims 1 to 5, characterized in that the content of silicon dioxide is less than 57 percent by weight.

7. The glass-fiber composition of any of claims 1 to 6, characterized in that the content of silicon dioxide is less than 56.5 percent by weight.

8. The glass-fiber composition of any of claims 1 to 7, characterized in that the content of aluminum oxide is at least 0.1 percent by weight.

9. The glass-fiber composition of any of claims 1 to 8, characterized in that the content of aluminum oxide is at least 0.5 percent by weight.

10. The glass-fiber composition of any of claims 1 to 9, characterized in that the content of phosphorus oxide is at least 0.1 percent by weight.

11. The glass-fiber composition of any of claims 1 to 10, characterized in that the content of boron oxide is more than 12 percent by weight.

12. The glass-fiber composition of any of claims 1 to 11, characterized in that the content of magnesium oxide is less than 2 percent by weight.

INTERNATIONAL SEARCH REPORT

national Application No
PCT/EP 95/01993

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 see claims; example 11	1,5, 8-10,12
A	US,A,5 055 428 (PORTER) 8 October 1991 see the whole document	1-12
A	GB,A,1 096 465 (UNITED STATES GYPSUM COMPANY) 29 December 1967 see claims; examples	1-12
A	EP,A,0 588 251 (SCHULLER INTERNATIONAL, INC.) 23 March 1994 see claims 1-3; tables 1,2	1-12

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[X] Further documents are listed in the continuation of box C.

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PCT/EP 95/01993

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	GLASTECHNISCHE BERICHTE, vol. 64, no. 1, January 1991 FRANKFURT DE, pages 16-28, XP 000178832 R. M. POTTER ET AL. 'Glass Fiber dissolution in a Physiological Saline Solution' see page 26 - page 27; table 2	1

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